

Express Mail Label No. EV342618999US  
Docket No. 51861

**U.S. PATENT APPLICATION**

Title: METHOD OF MEASURING COMPONENT LOSS

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## **METHOD OF MEASURING COMPONENT LOSS**

### **BACKGROUND OF THE INVENTION**

The present invention is directed to a method of measuring component loss from an electroless metal plating bath. More specifically, the present invention is directed to a method of measuring inert component loss from metal plating baths.

A plating facility is composed of a multitude of baths for electrodeposition of numerous metals. Many of such baths involve electroplating of metals requiring means for applying electric current to the baths to carry out the electrodeposition of metals. However, many plating shops also have tanks containing baths which, while also employing electrochemical processes for the electrodeposition of metals, do not require the application of electrical current to the bath. Such deposition processes are referred to as electroless plating. Electroless plating is based on the presence of a chemical reducing agent being added to the bath. Such chemicals supply electrons to substrate metals which transmit the electrons to the positively charged metal ions in the bath solution, reducing these ions to the metal in the same manner in which electric current reduces metal ions to metals in electrolytic or electrodeposition plating baths. The electroless plating of metals is of vast industrial importance and is used frequently in industrial metal plating.

Electroless plating produces several unique results. Whereas it is difficult to obtain uniform deposit thickness of metal plate in crevices and holes with electrolytic plating, it is automatic and routine with electroless plating. This attribute is critical to the electronics industry, in which printed circuit or printed wiring boards require uniform metal deposits plated into high aspect-ratio through-holes. Other properties and applications of electroless plating are deposits which may be produced directly upon nonconductors, deposits in which are often less porous than electrolytic plating, and also deposits which often have unique chemical, mechanical or magnetic properties (such as higher hardness and wear resistance).

Another characteristic of electroless plating is that it occurs on a catalytic surface; however the electroless plated deposit is always auto-catalytic, such that once the process has started it is self-perpetuating. Electroless plating baths are otherwise similar to electrolytic plating baths. Both are comprised of a combination of several different electrochemical constituents or additives. The constituents vary depending on the type of metal being plated, but may be broadly divided into consumable and non-consumable constituents. Consumable

constituents are additives that may decompose or are unstable during plating. Also, the properties of such constituents may change over time, thus rendering them unsuitable for their intended purpose. Whether or not a constituent is consumable or non-consumable may depend on the type of plating process employed, i.e., electroless or electrolytic, while some constituents are always consumed. For example metal is always a consumable constituent in an electrolytic bath and an electroless bath. However, electrolytic baths may employ soluble anodes of the same metal being plated so that the major metal concentration tends to remain fairly uniform. Also electrolytic baths do not have the requirements of a reducing agent as a major constituent because the external electric current performs the reducing agent function. Thus, consumption of reducing agents is not a problem in contrast to electroless baths. Stabilizers are typically consumed in electroless baths. Brighteners are consumed in both electrolytic and electroless baths. Chelating agents generally are not consumable in electrolytic or electroless baths.

Since the consumable constituents are in relatively low concentrations in electroless baths, it is crucial to follow in real-time concentration levels of the consumable constituents. If the consumable constituent levels drop too low, the rate of deposition becomes uneconomical, or the quality of the metal deposition is decreased. If the levels are too high, the catalytic selectivity for plating is lost and the metal “drops out” throughout the bath proper rather than being restricted to the desired surface.

Electroless baths are typically replenished with components designed to be added based on analysis of primary bath components, most commonly metal ions, but sometimes additionally reducing agent concentrations. Such bath components contain, in addition to the required amount of metal salts, reducing agents, stabilizers, inhibitors, brighteners (all of which may be consumed during plating), complexing agents and chelating agents. Solutions containing chelating agents typically are added to replace losses due to drag-out or bail-out. Drag-out is a loss of solution when workers retrieve plated substrates or other articles from plating baths. Invariably, when articles are removed from a bath solution, bath constituents are removed with the articles and any spilled bath solution. Bail-out is what is removed from a plating bath to prevent the bath or solution level from overflowing a tank. The amount of chelating agent added to replenish the bath is determined either on empirical experimentation or on an assumed level of bath or solution loss.

Some bath formulations employ a single chelating agent, which is readily analyzed, such as in electroless copper baths. Examples of such chelating agents include ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), N-(2-hydroxyethylenediaminetriacetic acid or nitriloacetic acid (NTA), monocarboxylic acids, dicarboxylic acids, ammonia, or tartaric acid salts. In such baths where one strong chelating agent is employed, the chelating agent concentration may be readily analyzed and then replenished. Such strong chelating agents include EDTA, DTPA, or NTA. However, when a bath composition contains multiple chelating agents at various concentrations or contains a weak chelating agent, analysis and replenishment of such chelating agents present a difficult problem of analysis such as in some electroless copper baths and many electroless nickel baths. Examples of weak chelating agents include many carboxylic acids such as maleic, citric acid or lactic acid. Nickel electroless plating baths typically employ weak chelating agents since the stronger chelating agents such as EDTA, DTPA, or NTA bind too strongly with nickel ions and prevent the nickel ions from depositing on substrates.

Electroless nickel baths typically use a complex mixture of three or more chelating agents to control plating rate and deposit properties such as phosphorous content and stress. No readily available analysis is known for such chelating systems. Complex approaches such as ion chromatography may be used, but such methods are not well suited to use in a bath control environment of an industrial setting. Ion chromatography often requires skilled workers, the process is time consuming, thus inefficient, and the ion chromatography apparatus and materials may be costly. Accordingly, such methods are undesirable in an industrial setting.

Since metal plating baths vary in formulation, a single replenishment formulation is not capable of managing widely varying levels of solution loss during bath operation. For example, an electroless nickel bath running a few hours per day, with a small plated area/solution volume ratio may require replenishment additions that are small compared to solution losses from evaporation. In contrast, baths running for continuous production, with a high plated area/solution volume ratio may require additions that are larger than the solution evaporation losses. In the latter situation, the bath volume increases during operation and over time bail-out of solution may be necessary to prevent the bath from overflowing from the work tank.

Baths using replenishment components that are more concentrated in metal ions and reducing agents are less likely to require bail-out, while baths using replenishment components

that are less concentrated in metal ions and reducing agents are more likely to require bail-out. More volume is added to the bath when a less concentrated replenishment is added to return components to their desired operating levels. Since this results in volume increases at a greater rate than evaporation, bail-out is needed to prevent overflow.

An electroless nickel product family, which is based on the use of nickel hypophosphite salts, is highly desirable for use in nickel electroless plating baths. Such nickel hypophosphite salts are desirable because they reduce the introduction of high levels of byproduct ions such as sodium or sulfate which otherwise are added to the electroless plating bath. Sodium and sulfate ions in sufficient amounts may interfere with the plating process by compromising the plating rate. Unfortunately, the nickel hypophosphite salt is less soluble than the alternative materials such as nickel sulfate or sodium hypophosphite and therefore employs more dilute replenishment components.

Workers running electroless nickel baths at high production throughputs may encounter solution bail-out. The bail-out leads to abnormal losses of chelating agents. If the loss of chelating agents is too great, insoluble nickel salts may precipitate out of the bath rendering the electroless process inefficient or inoperable. In order to replace the chelating agent losses, workers add some stock solution of bath components containing the chelating agent. However, calculating the exact amount of chelating agent loss and therefore the appropriate quantity of stock solution to add is difficult. In practice, an empirical approach is often used (i.e. add X% of the chelating agent per bath cycle/metal; metal turn over). The value X is varied, based on the responses of bath failure due to chelating agent loss (solution white out from precipitation of insoluble nickel salts if adds are too low) and to bath failure due to excessive chelating agent in the bath (metal plating rate loss). The empirical approach is an inexact method, which does not handle well variable levels of solution bail-out due to work load variation. Accordingly, there is a need for an improved method of determining the amount of chelating agent in metal plating baths, in particular electroless nickel metal plating baths.

#### SUMMARY OF THE INVENTION

The present invention is directed to a method including the steps of providing a metal plating composition with known amounts of components; operating the metal plating composition to deposit a metal on a substrate; analyzing an aliquot of the metal plating composition to determine an amount of an inert indicator from the metal plating composition;

and correlating a change in the amount of the inert indicator to a change in an amount of an inert metal plating composition component. After the change in the amount of the inert metal plating composition component is determined, the initial amount of the inert component may be replenished in the metal plating composition to restore the inert component to an appropriate level.

During operation of metal plating compositions or baths, bath components are broken down or degraded, or lost due to drag-out, bail-out or solution spillage. To maintain optimum performance of the metal plating compositions, workers replenish lost composition components. While inert components such as chelating agents do not degrade or breakdown, they may be lost during drag-out, bail-out or spillage. Loss of such inert chelating agents may result in the undesirable precipitation of other bath components such as metal ions resulting in the decline of metal plating performance. Thus, workers attempt to restore the amount of chelating agent to its initial or optimum operating level. Conventional methods have not been satisfactory for adequately monitoring inert component loss and replenishing the loss to its initial or optimum levels in many plating compositions. By adding an inert indicator component to a metal plating composition, workers may readily monitor and restore inert metal plating composition components, such as chelating agents, to their initial or optimum levels by correlating the change in the inert indicator component to the change in the one or more inert composition components. A change in concentration of the inert indicator may be determined by any suitable analytical method or apparatus known in the art. Accordingly, the method of the present invention provides for a more accurate determination of inert component loss than conventional methods, and eliminates or at least reduces the uncertainty of incorrect replenishment of inert metal plating components. Thus, bath performance may be readily maintained at optimum performance.

A primary objective of the present invention is to provide a method for monitoring and replenishing inert metal plating composition components.

Another objective of the present invention is to provide a method for direct analysis of inert components of a metal plating composition.

A further objective of the present invention is to provide a method of direct analysis of chelating agents in electroless plating baths.

Still yet a further objective is to provide a method of direct analysis of chelating agents in electrolytic plating baths.

Additional advantages may be readily determined by a person of skill in the art after reading the detailed description and the appended claims.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a method for determining amounts of inert components in metal plating compositions or baths by measuring the concentration change of an inert indicator added to the metal plating composition and correlating the change in the concentration of the inert indicator component to one or more known inert components in the metal plating composition. The amounts of each component added to the metal plating composition are known when the bath is made including all of the inert components of the plating composition. Since inert plating composition components do not break down or degrade during operation of the bath or storage of the bath prior to use, loss or change in concentrations of inert components and inert indicators of a metal plating composition are due to either drag-out, bail-out or spillage. Accordingly, when the amount of an inert indicator changes by a percentage weight range or concentration range, the percentage weight range or concentration range of an inert component may be expected to change by the same weight percentage or concentration ratio as the inert indicator. For example, when the loss of the inert indicator is 50% from its initial concentration, the concentration of the inert component of the metal plating bath also is 50% of the initial concentration because neither component is consumed in the plating process. Thus, the change in the amount of inert indicator may be correlated to the change in the amount of inert metal plating composition component. When the change in the amount of inert component is determined, workers may replenish the metal plating composition with a sufficient amount of the inert component to return it to its desired operating level. Metal plating compositions within the scope of the present invention include both electrolytic and electroless metal plating compositions.

One or more aliquots or analytical samples of a metal plating composition or bath may be taken at any suitable time or at suitable time intervals according to the discretion of workers to determine the amount of inert indicator in the metal plating composition and correlate the amount of inert indicator to determine the amounts of inert metal plating bath components. In one embodiment of the invention, an inert indicator may be added to a metal plating composition initially or prior to metal plating operation, and monitoring the progress or loss of the concentration of the inert indicator at various time intervals to determine the amount of inert

components that may be replenished to the bath. In another embodiment of the invention, inert indicator may be added to the metal plating composition to return it to its initial concentration after each analysis. The concentration change of the inert indicator may then be correlated to changes in the inert components of the metal plating composition.

Time intervals for taking aliquots for inert indicator analysis may vary depending on the specific composition of the metal plating bath and the duration of the metal plating process. Workers operating the baths may determine their own preferred time intervals based on experience with a particular bath composition and operating times for the baths. For example, a number of nickel and copper electroless plating compositions are monitored for inert components every one to four hours due to bail-out to prevent bath or tank overflow. Also some evaporation occurs during the electroless metal plating process resulting in undesirably concentrating some of the bath components.

Aliquots may be analyzed for inert indicators by any suitable method known in the art for a given inert indicator. Examples of suitable methods for analysis include, but are not limited to, flame photometry, absorption analysis, atomic absorption spectroscopy (AA), inductive coupled plasma analysis (ICP), liquid X-ray fluorescence, electrochemical measurements (such as cyclic voltammetry), ultra violet (UV) analysis, visible light analysis, or nuclear magnetic resonance (NMR). All such methods are well known in the art as well as procedures used to analyze aliquots for a particular chemical compound or ion. A preferred method of analyzing aliquots is by atomic adsorption spectroscopy because the process is accurate and readily available in a typical plating shop.

Inert indicators which are suitable for practicing the invention are compounds or ions (cations or anions) that do not break down, degrade or complex with electroless metal plating composition components, or electrolytic metal plating composition components that may mask the concentration of the inert indicator in the composition during use of the metal plating composition. Inert indicators also are soluble in the solvent of the metal plating composition and do not interfere with the plating process, or do not appreciably interfere with the plating process such as to render the plating process undesirably inefficient to workers. Inert indicators typically are inert ions such as cations or anions. Examples of suitable inert indicators include, but are not limited to, alkali metal ions such as lithium, sodium, potassium, rubidium, or cesium. Lithium, rubidium and cesium are more preferred over sodium and potassium because many metal plating



baths contain sodium or potassium salts which may interfere with an accurate analysis of the concentration of the inert indicator. When a metal plating bath contains sodium or potassium salts, such ions are avoided and another ion, which is not part of the operating bath composition, is employed as the inert indicator.

Inert indicator ions may be added to the metal plating compositions as their soluble salts. For example alkali metal salts may be added to the electroless metal baths as sulfate, sulfamate, nitrate, halide, carboxylate, or hypophosphite salts, or mixtures thereof. Sulfate, sulfamate, nitrate, halide, carboxylate or hypophosphite salts of lithium are highly desirable because lithium compounds are not typically used as an electroless bath component as well as an electrolytic bath component, and lithium is accurately analyzable with many known analytical processes. Another suitable ion that may be employed as an inert indicator is an yttrium (Y) ion. Yttrium ions may be added to the electroless or electrolytic baths as any soluble salt. Examples of such salts include, but are not limited to sulfate, sulfamate, nitrate, halide, or carboxylate salts of yttrium, or mixtures thereof. Yttrium is a highly desirable inert indicator when measuring inert indicator concentrations by ICP or AA methods.

Inert indicators are added to metal plating compositions in sufficient amounts such that the compound or ion that performs the indicator function is at a concentration of from 1 ppb (parts per billion) to 1000 ppm (parts per million), preferably from 5 ppm to 500 ppm, most preferably from 10 ppm to 250 ppm. Such ranges are analyzable with various analytical methods, and do not interfere with metal plating processes to render the processes inefficient, or compromise the quality of plated metal layers.

Inert metal plating composition components may be replenished in the metal plating composition by any suitable method. The inert components may be replenished by adding concentrates, solutions, suspensions or dry powders of the components to the bath. Inert components typically included in electroless and electrolytic metal plating compositions or baths include, but are not limited to, chelating agents. Chelating agents are included in electroless and electrolytic metal plating baths to solubilize another bath component which otherwise may precipitate out of the bath to render the metal plating process inefficient or inoperable. Typically chelating agents are employed to solubilize metal ions such as  $\text{Hg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Au}^{2+}$ , or  $\text{Cr}^{3+}$ . Accordingly, such chelating agents may be an important component of the electroless and electrolytic metal plating composition. Such

chelating agents may be employed in various concentrations in metal plating compositions. The amounts and types employed vary from composition to composition because both electroless and electrolytic metal plating baths can be specific in composition depending on the type of metal in the bath, and the type of substrate to be metal plated. Thus, metal plating compositions may contain numerous components and be complex in their make-up.

Examples of suitable inert complexing agents used in metal plating baths include, but are not limited to, monocarboxylic acids, dicarboxylic acids, ammonia, tartaric acid salts such as Rochelle salts, monoamines, diamines, triamines, amino acids, boric acid (such as Watts Nickel formulation), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), N-(2-hydroxyethyl) ethylenediaminetriacetic acid or nitriloacetic acid (NTA). The foregoing list of complexing agents is not exhaustive, but lists some of the more commonly employed chelating agents in metal plating baths. Such chelating agents may be employed individually or as mixtures of two or more in a given bath. Chelating agents may be employed in metal plating compositions or baths in amounts of from 10 ppm to 1000 ppm, more typically from 100 ppm to 500 ppm. The choice of a chelating agent or combination of chelating agents varies depending on the metal and bath composition. For example copper electroless and electrolytic plating baths may employ strong chelating agents such as EDTA, DTPA, NTA, or mixtures thereof in addition to the weaker chelating agents such as monocarboxylic acids, dicarboxylic acids, ammonia, tartaric salts, amino acids, monoamines, diamines, triamines, or mixtures thereof. Nickel electroless and electrolytic plating baths employ weaker chelating agents such as monocarboxylic acids, dicarboxylic acids, ammonia, tartaric salts, amino acids, monoamines, diamines, triamines, or mixtures thereof. Examples of weak chelating agents that are commonly employed with nickel plating baths include lactic acid, citric acid, maleic acid, propionic acid, glycine, alkanolamines, or mixtures thereof. Such strong chelating agents such as EDTA, DTPA and NTA form such strongly bonded complexes with nickel that they are not desirable for use in a nickel plating bath.

As discussed above a metal plating bath is specifically formulated depending on the metal and substrate. Accordingly, a choice of an inert chelating agent or combination of inert chelating agents may vary from one bath to another. Formulation of a metal plating bath may involve experimentation by workers in the art to find an appropriate combination of components.

The analytical method of the invention may be employed to determine inert components such as chelating agents in numerous electroless and electrolytic plating compositions. For example the analytical method may be used to monitor inert components in electroless and electrolytic copper, copper alloy, nickel, palladium, gold, silver, chromium, cobalt, lead, tin, cadmium, platinum, rhodium, or zinc baths. In addition to inert components such as chelating agents and a source of metal ions used to metal plate a substrate, metal plating compositions also include, but are not limited to, reducing agents such as formaldehyde, sodium hypophosphite or amino boranes, stabilizers to prevent solution breakdown, accelerators, brighteners, and buffers to maintain a desired pH range. Electrolytic metal plating compositions may include, but are not limited to, brighteners, buffers, levelers, stabilizers, accelerators, and carriers. Amounts of each component and the specific type of components employed in a bath may vary from bath to bath depending on the type of metal to be deposited on a substrate. Such baths often are aqueous based, but organic solvents may be employed in some formulations. The pH ranges of the baths may range from 0 up to 14. Typically many baths have a pH range of from 4 to 14. Various specific bath compositions are well known in the art and describing the various electroless and electrolytic metal plating compositions is too extensive and unnecessary to explain how to make and use the present invention to a person of skill in the art.

An example of an electrolytic metal plating composition may have the following components: an aqueous acid solution of the metal to be plated such as copper, or nickel, proprietary additives from groups such as dyes, surfactants, chelating agents, brighteners, and leveling agents. Acids that may be employed in the formulation include, but are not limited to, acids having a high ionic dissociation constant for maximum conductivity such as sulfuric acid, fluoroboric acid, or sulfamic acid. Examples of suitable dyes include methylene blue, methyl violet, and other N-heterocyclic compounds; triphenyl methane dyes, aromatic amines, imines and diazo compounds. Suitable surfactants include non-ionic surfactants such as alkylphenoxy polyethoxyethanols, such as octylphenoxy, and polyethoxyethanol. Surfactants include wetting agents and water-soluble organic compounds such as compounds containing multiple oxyethylene groups such as block polymers of polyoxyethylene and polyoxypropylene.

Exemplary nickel electroless plating baths may have the following components: nickel chloride, sodium hypophosphite, reducing agent, sodium citrate and sodium acetate. A high deposition rate electroless nickel bath includes nickel chloride, sodium hypophosphite, lactic

acid, propionic acid and a trace amount of lead ion. Another high deposition rate electroless nickel bath includes nickel hypophosphite, reducing agent, brightener, buffer, and two or more chelating agents.

While the analytical method of the present invention may be employed to monitor the concentration of inert compounds in numerous electroless and electrolytic metal plating compositions, the method of the present invention is especially suitable for determining or monitoring the amount of inert components in a nickel hypophosphite electroless metal plating composition. Such compositions include two or more chelating agents to solubilize nickel and keep it in solution, thus employing an inert indicator such as an inert indicator ion provides a more accurate determination of inert component concentrations during plating. Additionally, nickel hypophosphite salt is less soluble than alternative materials such as nickel sulfate in combination with sodium hypophosphite, and therefore employs more dilute replenishment components. If replenishment of the inert chelating agents is too low, white out from precipitation of insoluble nickel salts occurs. The once clear plating bath becomes turbid to a milky white/green in appearance due to the precipitation of colloidal nickel salts. The precipitate may deposit at the bottom of a plating bath tank to form caked colloidal nickel salts. The precipitate may be eliminated by reducing the electroless plating composition to room temperature (18° C to 21° C), or by lowering the pH of the plating composition to below 4 followed by raising the pH to 5 or above. However, preemptive measures are more desirable because methods to eliminate the colloidal nickel precipitate are not always reliable, thus the contaminated bath may have to be replaced with an entire new plating bath. Accordingly, plating efficiency is compromised and costly materials are wasted.

If too much of the inert component is added to the composition, the excess may cause other components to precipitate out of solution, thus compromising the performance of the electroless plating process. Accordingly, to avoid adding too much or too little of inert replenishment components, a more accurate determination of inert component loss is highly desirable.

The method of the present invention provides for a direct method of determining inert component concentrations, thus providing a more accurate method than conventional methods. The method also enables workers to use preemptive measures to prevent the formation of colloidal nickel precipitates in nickel plating compositions. By periodically measuring inert

indicator concentrations during plating processes, workers may add sufficient amounts of depleted inert components to plating compositions to prevent precipitates from forming in the plating compositions. Replenishment periods may vary from plating composition to plating composition, and minor experimentation may be involved in determining at what point replenishment is to take place for a given plating composition. As mentioned above plating compositions may be specific in their components. Some plating compositions are more sensitive to component changes than others, thus replenishment periods may be specific and are determined by workers operating a particular plating composition. In general, replenishments are added to plating compositions before a loss of one or more inert components may compromise a plating process.

In general, replenishments are added to plating compositions when 50% by weight of an inert component is lost, typically from 10% by weight to 30% by weight of an inert component is lost, more typically when 15% to 20% by weight is lost. For example to prevent colloidal nickel precipitation, replenishing an electroless nickel plating composition with inert chelating agents may take place after 10% by weight to 50% by weight of the chelating agents are lost from the plating composition. Typically replenishments are added when an electroless nickel plating composition loses 30% by weight to 50% by weight of the chelating agents. More typically replenishments are added when the electroless nickel plating composition loses from 15% to 20% by weight of the chelating agents.

The analytic method of the present invention may be used to analyze electrolytic and electroless metal plating compositions for electrolytic and electroless plating in printed circuit boards including metallization of through-hole surfaces, plating on ceramic materials such as ceramic resistors and ceramic circuit boards, and plating of integrated circuits.

The following examples are intended to further illustrate the invention, but are not intended to limit the scope of the invention.

#### Example 1

Nickel hypophosphite is prepared by dissolving nickel carbonate in hypophosphorous acid at room temperature until a saturated solution of  $\text{NiH}_2\text{PO}_2$  is formed. Analysis indicates that the supernatant liquid contained 35 grams/liter of nickel.

A sufficient amount of nickel hypophosphite prepared as mentioned above is dissolved in an aqueous solution containing electroless metal plating components to make the aqueous electroless nickel plating bath disclosed in the table below.

Nickel hypophosphite	20 grams/liter
Citric acid	14 grams/liter
Lactic acid	10 grams/liter
Glycine	6 grams/liter
Thiourea	5 ppm

A sufficient amount of lithium sulfate is added to the electroless nickel plating solution such that the final concentration of the lithium ion in solution is 100 ppm. The lithium ion is employed as an inert indicator to monitor the inert chelating agents citric acid, lactic acid and glycine during electroless nickel plating.

An apparatus is constructed with a 10 liter solution capacity featuring continuous cascading solution flow with filtration at a rate of 3 liters per minute and heating with a 500 watt Teflon® heater panel. The relatively high flow rate is employed to preclude local overheating, which may lead to spontaneous nickel deposition on the heater. Two 20 cm by 23 cm laminated copper/epoxy glass panels serve as plating substrates for assessing the deposit appearance and for measuring the amount of nickel deposit by weight gain. Each panel is pretreated to render them acceptable to receiving a catalyst for nickel deposition. The electroless bath is heated for 2 hours before a plating temperature of 85° C is reached and nickel deposition begins.

After 8 hours of electroless plating, the electroless nickel plating bath appears clear. There is no sign of a milky white/green precipitate of colloidal nickel salts in the bath. To avoid formation of the milky white/green precipitate of colloidal nickel salts, workers remove one aliquot of the electroless nickel plating bath to analyze the lithium concentration to determine the amount of lithium and chelating agents lost from the bath due to spillage and drag-out. The aliquot is analyzed twice by atomic absorption with an atomic absorption spectrometer employing conventional methods. An average value for the concentration of lithium is determined from the aliquot. Analysis results show that the lithium concentration is reduced by 20% of its initial bath concentration. Since citric acid, lactic acid and glycine are inert chelating agents, the concentrations of each decrease by 20% of their initial bath concentrations. Thus, the citric acid, lactic acid and glycine concentrations in the bath after 8 hours are 11.2 grams/liter, 8 grams/liter, and 4.8 grams/liter, respectively.

A sufficient amount of stock solution of citric acid, lactic acid and glycine is added to the bath to raise the concentration of each chelating agent by 20% to bring the concentration of each chelating agent to its initial bath concentration and to prevent colloidal nickel precipitation. Accordingly, lithium is a suitable inert indicator for correlating the concentrations of inert chelating agents in electroless nickel plating baths.

After the plating process is complete, each copper/epoxy glass panel is weighed. Each panel has the same weight indicating uniform nickel plating of each panel. Each panel also has a smooth planar surface.

### Example 2

Nickel hypophosphite is prepared by dissolving nickel carbonate in hypophosphorous acid at room temperature until a saturated solution of  $\text{NiH}_2\text{PO}_2$  is formed. Analysis indicates that the supernatant liquid contains 35 grams per liter of nickel.

A sufficient amount of the nickel hypophosphite is added to a solution containing electroless plating components to form an electroless nickel plating composition shown in the table below.

Nickel hypophosphite	30 grams/liter
Lactic acid	10 grams/liter
Acetic acid	4 grams/liter
Propionic acid	8 grams/liter
Glycine	35 grams/liter
Thiourea	25 ppm

Lithium sulfate is added to the electroless nickel plating bath to provide a lithium ion concentration of 200 ppm. The lithium ion acts as an inert indicator for measuring the concentrations of the inert chelating agents lactic acid, acetic acid, propionic acid and glycine in the bath. The inert chelating agents keep the nickel in solution during electroless plating.

An apparatus is constructed with a 10 liter solution capacity featuring continuous cascading solution flow with filtration at a rate of 3 liters per minute and heating with a 500 watt Teflon® heater panel. The high flow rate is employed to preclude local overheating, which may lead to spontaneous nickel deposition on the heater. Two 20 cm by 24 cm laminated copper/epoxy glass panels serve as plating substrates for assessing the deposit appearance and for measuring the amount of nickel deposit by weight gain. Each panel is pretreated to render

them acceptable to receiving a catalyst for nickel deposition. The bath is heated for 2 hours to reach a nickel plating temperature of 85° C. Nickel plating is performed over 8 hours.

After 2 hours of nickel plating, no precipitate of colloidal nickel salts is observed by workers. As a preemptive measure to avoid formation of the colloidal nickel salts workers take one aliquot from the plating bath to determine the amount of lithium lost during the first 2 hours of bath operation. The aliquot is analyzed with an NMR and the lithium concentration is determined. The lithium concentration after 2 hours of bath operation is reduced by 10% of the initial concentration of the electroless plating bath. The loss of lithium is due to drag-out and spillage. Accordingly, the concentrations of lactic acid, acetic acid, propionic acid and glycine also decrease by 10% of their initial bath concentrations. Thus, the concentrations of lactic acid, acetic acid, propionic acid and glycine after 2 hours of plating are 9 grams/liter, 2.6 grams/liter, 7.2 grams/liter, and 31.5 grams/liter, respectively.

A sufficient amount of stock solution of lactic acid, acetic acid, propionic acid and glycine is added to the electroless nickel plating bath to raise the concentrations of each chelating agent by 10%. In addition to returning the concentrations of each chelating agent to their initial bath concentrations, a sufficient amount of stock solution of lithium sulfate is added to the bath to return the lithium ion concentration to 200 ppm.

Analysis of lithium ion concentration is performed at 2 hours intervals throughout the electroless plating process with additions of chelating agents and lithium sulfate to the plating bath to monitor and maintain chelating agent concentrations in sufficient amounts to maintain the solubility of nickel. Accordingly, lithium ions may be employed to determine the concentration changes in inert chelating agents in electroless plating baths and assist in maintaining efficient operation of electroless plating.

After the plating process is completed each copper/epoxy glass panel is weighed. Each panel weighs the same indicating uniform nickel plating of each panel. Also each panel has a smooth planar surface.

### Example 3

A stock solution of nickel hypophosphite is prepared as disclosed in Examples 1 and 2 above. A sufficient amount of the nickel hypophosphite from the stock solution is combined with electroless metal plating components to make an electroless metal plating composition as shown in the table below.



Nickel hypophosphite	20 grams/liter
Sodium citrate	5 grams/liter
Propionic acid	10 grams/liter
Thiourea	20 ppm
Glycine	20 grams/liter

A sufficient amount of yttrium sulfate is added to the electroless nickel plating bath to provide an yttrium ion concentration of 50 ppm. The yttrium ion is used as the inert indicator ion to measure the concentrations of the three inert chelating agents citrate, propionic acid and glycine.

The apparatus employed and the substrates to be plated are the same as described in Examples 1 and 2 above. Nickel plating is performed for 10 hours with one aliquot removed from the plating bath every 2 hours to determine the yttrium concentration in the plating bath. After every 2 hours interval the yttrium concentration is found to decrease by 15% by weight of its initial concentration due to drag-out and spillage of the plating bath. A 15% loss of each chelating agent also is believed to occur. To maintain the initial concentration of each chelating agent and to prevent precipitation of the milky white/green insoluble nickel salts from the bath, each chelating agent is replenished in amounts of 15% after each 2 hours period. No white precipitate is observed during the entire plating process, and after the plating process is complete after 10 hours, each panel has a uniform and smooth nickel layer.

Accordingly, yttrium ions may be employed to monitor the concentration change of inert chelating agents in electroless metal plating baths. Thus, the method of the present invention provides an improvement in electroless metal plating.